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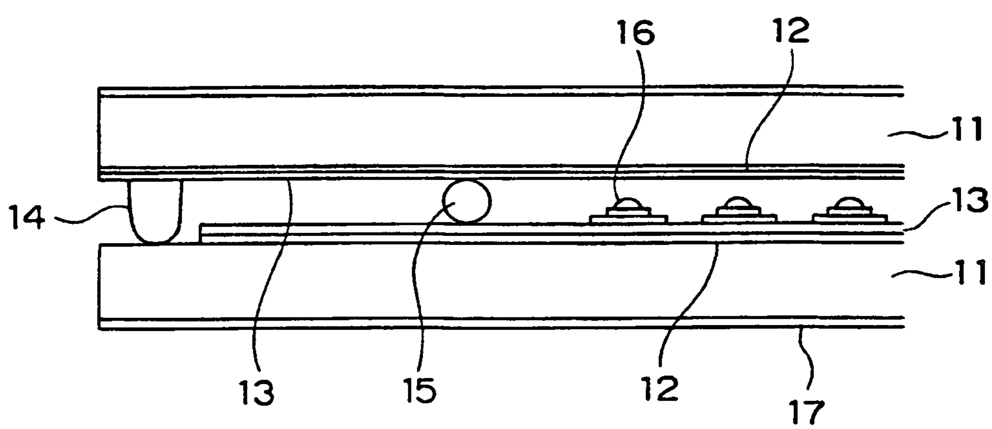
(54) Title: GLASS SUBSTRATE AND GLASS COMPOSITION FOR USE IN A LIQUID CRYSTAL PANEL



(57) Abstract: In liquid crystal panel glass suitable for a polysilicon TFT substrate, a strain point, specific gravity, and a Young's modulus are determined to obtain pertinent solubility, a light weight, and strength for the polysilicon TFT substrate. Specifically, the strain point is not lower than 680°C while the specific gravity is not higher than 2.45, and the Young' modulus is not smaller than 7600GPa. The glass may include a combination of SiO_2, B_2O_3, Al_2O_3, and MgO.

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DESCRIPTION

GLASS SUBSTRATE AND GLASS COMPOSITION FOR USE IN A LIQUID CRYSTAL PANEL

Background of the Invention:

This invention relates to a glass substrate and a glass composition which is for use in a liquid crystal panel and which will be often simply called a glass substrate and a glass composition throughout the instant specification, respectively.

Recently, a liquid crystal panel or display tends to be widely used in various fields. For example, such a liquid crystal panel has been also used in a laptop computer and a digital video disk (DVD) player. From this fact, it is required that the liquid crystal panel is light in weight, compact in size, and can display very fine images.

To this end, provision must be made about a liquid crystal panel glass composition which has a high strain point, a light weight, and a high strength such that thin film transistors (TFT) can be formed on the liquid crystal panel.

Herein, it is to be noted that conventional TFTs are classified into amorphous silicon TFT and polysilicon TFT. Among others, the amorphous TFT can realize a wide screen and can be manufactured at a low temperature process. Therefore, the amorphous TFT has thus far been widely used in comparison with the polysilicon TFT. However, such amorphous TFT inevitably makes a drive circuit complex in structure due to characteristics of materials used therein and, as a result, make fine integration difficult.

On the other hand, the polysilicon TFT is advantageous in that it is possible to simplify a drive circuit in structure and, therefore, to form pixels at a

high density. However, the polysilicon TFT has a drawback that a high temperature process is necessary on manufacturing the polysilicon TFT. Although recent studies have been directed to a polysilicon TFT which can be manufactured at a low temperature, they have reported that a process between 600°C and 650°C is indispensably necessary.

Under the circumstances, the liquid crystal panel glass has been usually formed by quartz glass which has high stability such that neither thermal shrinkage nor deformation takes place. Such quartz glass is suitable for the liquid crystal panel because of its properties but it is expensive.

Alternatively, glass which includes no alkali components and which will be called non alkali glass has been also used as the liquid crystal panel glass. However, no proposals have been disclosed yet about non alkali glass having a high strain point which can withstand the manufacturing process of the polysilicon TFT.

In addition, it is preferable that the liquid crystal glass is light in weight because the liquid crystal panel has been often utilized in portable devices, such as a mobile device, a laptop computer. Moreover, it is required that the liquid crystal panel glass has low specific gravity and low flexibility so as to easily handle the glass during a manufacturing process and a test process. Such low flexibility leads to a high Young's modulus.

In general, it might be predicted that such glass which fulfills all of the requirements mentioned above has very bad solubility and a very high solution temperature. This might brings about a difficulty in refinement and uniformity. In addition, no disclosure has been made about a glass composition and a glass substrate which has a strain point not lower than 680°C and a specific modulus not lower than 31 GPa, where the specific modulus is given by a ratio of Young's ratio to specific gravity.

Summary of the Invention:

It is an object of this invention to provide a liquid crystal panel glass substrate or composition which is suitable for a polysilicon TFT substrate and which has a high strain point not lower than 680°C.

It is another object of this invention to provide a liquid crystal panel glass substrate or composition of the type described, which is light in weight and high in strength.

It is still another object of this invention to provide a liquid crystal panel glass substrate or composition of the type described, which has good solubility and which is good in refinement and uniformity.

It is yet another object of this invention to provide a liquid crystal panel glass substrate or composition of the type described, which is excellent in devitrification proof and refining or degassing and which is substantially free from stria.

It is anther object of this invention to provide a glass substrate or composition of the type described, which has a high specific modulus not lower than 31 GPa.

According to this invention, liquid crystal panel glass has a strain point not lower than 680℃, specific gravity not higher than 2.45, and a Young' modulus not smaller than 76GPa. Preferably, the liquid crystal panel glass has the strain point not lower than 690℃, the specific gravity not higher than 2.42, and the Young' modulus not smaller than 77GPa.

Brief Description of the Drawing:

Fig. 1 shows a schematic sectional view of a liquid crystal display which uses a pair of glass substrates according to this invention.

Description of Preferred Embodiments:

According to the inventor's experimental studies, it has been found out that liquid crystal panel glass substrate or composition for polysilicon TFT might have a strain point not lower than 680℃ (preferably, 690℃), specific gravity not

higher than 2.45 (preferably, 2.42), and a Young's modulus not lower than 76 GPa (preferably, 77 GPa). This shows that a specific modulus can be calculated because the specific modulus is given by a ratio of the Young's modulus (E) to specific gravity. By using the above-mentioned Young's modulus and specific gravity, the glass substrate or composition according to this invention has the specific modulus not lower than 31 GPa.

In order to calculate the Young's modulus (E), an annealed glass specimen having a density (ρ) and a size of 20x20x100mm is prepared and introduced into a chamber kept at a high temperature. Thereafter, measurement is made about a longitudinal velocity (V_L) of a ultrasonic wave of 6MHz. In this event, the Young's modulus is given by:

$$E = (4G2 - 3GV_L^2 \rho)/(G-V_L^2 \rho),$$

where G is representative of a shear modulus or a modulus of rigidity.

In addition, as the specific gravity becomes small, it is possible to reduce a warp or deformation of the glass substrate when it is assembled in a liquid crystal display. This is because an amount of the warp (W) is given by:

$$W = (L^4 g \rho (1- \nu^2))/(6.4Et^2),$$

where L and t is representative of a length and a thickness of the glass specimen, respectively, and ν, a Poisson's ratio and the warp W is mainly dependent on ρ/E. This means that the warp (W) is decreased in dependency upon the specific gravity (ρ).

The above-mentioned strain point, specific gravity, and Young's modulus have been realized by glass which comprises 67-72mol% of SiO_2, 6-10mol% of B_2O_3, 9-15mol% of Al_2O_3, 3-13.5mol% of MgO, 0-6mol% of CaO, 0-

0.3mol% of SrO, 0-0.2mol% of BaO, and 0-0.5mol% of As_2O_3. In addition, it has been confirmed that each of Sb_2O_3 and SnO_2 may be added up to 1mol%.

In addition, it is preferable in the glass substrate or composition that a first sum amount of Al_2O_3, MgO, and CaO falls within a range between 20mol% and 24mol%. Moreover, it has been found out that a second sum amount of SiO_2, B_2O_3, Al_2O_3, MgO, and CaO (namely, $SiO_2+B_2O_3+Al_2O_3+MgO+CaO$) may be not smaller than 97 mol%, preferably, 98.5 mol%, and more preferably, more than 99 mol%. At any rate, the second sum amount may fall within a range between 97mol% and 99.5mol%. A first ratio of Al_2O_3 to B_2O_3, namely, Al_2O_3/B_2O_3 may be present in mol ratio between 1.1 and 2.2 while a second ratio of the first sum amount ($Al_2O_3+MgO+CaO$) to a third amount of ($SiO_2+B_2O_3$) may be present in mol ratio between 0.25 and 0.32. This shows that the mol ratio of $(Al_2O_3+MgO+CaO)/(SiO_2+B_2O_3)$ may be not smaller than 0.25 on the condition that $Al_2O_3+MgO+CaO$ is not smaller than 20 mol%. More preferably, $Al_2O_3+MgO+CaO$ may fall within a range between 20-22.5 mol% while the mol ratio of Al_2O_3/B_2O_3 is between 1.1 and 1.7. In this event, it is preferable that ($SiO_2+B_2O_3+Al_2O_3+MgO+CaO$) is not lower than 99 mol% and $(Al_2O_3+MgO+CaO)/(SiO_2+B_2O_3)$ is between 0.25 and 3.0.

Herein, it is to be noted that As_2O_3 or alkali metal oxide may not substantially be included in the glass. The glass may preferably have an average thermal expansion coefficient not greater than 35×10^{-7}/°C within a temperature range between 100 and 300°C. More preferably, the thermal expansion coefficient may be not greater than 31×10^{-7}/°C within a temperature range between 100 and 300°C.

In addition, Table shows any other examples 1 through 4.

Table

	Examples				
	1	2	3	4	5
	mol%	mol%	mol%	mol%	mol%
SiO_2	69	72	68	69	70
B_2O_3	8	7	9	8	7
Al_2O_3	13	11	11	9	11
MgO	5	5	7	13.5	9
CaO	4	4	4	0	2
SrO	0.3	0.3	0.3	0	0.4
BaO	0.2	0.2	0.2	0	0.1
As_2O_3	-	-	-	-	-
Sb_2O_3	-	-	0.5	0.5	-
SnO_2	0.5	0.5	-	-	0.5
Total	100	100	100	100	100
Al_2O_3+MgO+CaO	22	20	22	22.5	22
Al_2O_3/B_2O_3	1.63	1.57	1.38	1.13	1.57
$SiO_2+B_2O_3+Al_2O_3$+MgO+CaO	99	99	99	99.5	99
(Al_2O_3+MgO+CaO)/($SiO_2+B_2O_3$)	0.286	0.253	0.286	0.292	0.286
Strain Point (℃)	706	695	695	690	700
Specific Modulus (GPa)	32.8	32.4	32.6	33.4	33.3
Specific Gravity	2.41	2.38	2.41	2.39	2.40
Young's Modulus (GPa)	79	77	78.5	80.5	80
α 100-300 (x 10^{-7}/℃)	27	28	30	31	29
Viscosity at 1500℃ (poise)	250	300	200	200	29-
Presence or Absence of Crystals in Glass Obtained After Heat Treatment of 1100℃ x 18 h	ab-sence	ab-sence	ab-sence	ab-sence	ab-sence

Taking the above into consideration, it may be concluded that the glass substrate or the glass composition for the liquid crystal panel may comprise 65-75mol% of SiO_2, 6-11 mol% of B_2O_3, 8-15 mol% of Al_2O_3, 3-15 mol% of MgO, 0-8 mol% of CaO, 0-1 mol% of SrO, 0-1 mol% of BaO, 0-1 mol% of As_2O_3, 0-1 mol% of Sb_2O_3, and 0-1 mol% of SnO_2. Furthermore, the first sum amount (Al_2O_3+MgO+CaO) might fall within a range between 20 mol% and 25 mol% while the first ratio (Al_2O_3/B_2O_3) is present within a range between 1.1 and 2.2. Likewise, the second sum amount ($SiO_2+B_2O_3+Al_2O_3$+MgO+CaO) may not be smaller than 98.5 mol% while the second ratio (the first sum amount to the third sum amount of SiO_2 and B_2O_3), namely, (Al_2O_3+MgO+CaO)/($SiO_2+B_2O_3$) may not be smaller than 0.25.

More desirably, the glass substrate or composition may comprise, by mol%, 68-72% of SiO_2, 7-9% of B_2O_3, 9-13% of Al_2O_3, 5-13.5% of MgO, 0-3.4% of CaO, 0-0.4% of SrO, 0-0.1% of BaO, 0-0.5% of As_2O_3, 0-0.5% of Sb_2O_3, and 0-0.5% of SnO_2.

The limitation reasons enumerated above will be listed below.

In order to accomplish the strain point not lower than 670℃, not less than 8mol% of Al_2O_3 and not greater than 11mol% of B_2O_3 are to be included in the glass with a first ratio of Al_2O_3 to B_2O_3 (Al_2O_3/B_2O_3) kept in a range not be smaller than 1.1. As to the strain point, it is preferable that alkali metal oxide may not be included in the glass.

The specific gravity which is not greater than 2.45 can be achieved by keeping the first sum amount (Al_2O_3+MgO+CaO) within a range which is not greater than 25mol% and by keeping the second sum amount ($SiO_2+B_2O_3+Al_2O_3$+MgO+CaO) within a range which is not smaller than 97mol%.

Furthermore, the Young's modulus which is not smaller than 76GPa can be obtained when the first sum amount (Al_2O_3+MgO+CaO) is not smaller than

20mol% and when the second ratio $(Al_2O_3+MgO+CaO)/(SiO_2+B_2O_3)$ is equal to or greater than 0.25.

The devitrification proof can be maintained when SiO_2 and B_2O_3 are equal to or greater than 65mol% and 6mol%, respectively, on the assumption that Al_2O_3 does not exceed 15mol%. In this event, it is necessary to keep the first ratio (Al_2O_3/B_2O_3) equal to or less than 2.2. CaO, SrO, and BaO are added up to 8mol%, 1mol%, and 1 mol%, respectively.

The solubility can be desirably kept when SiO_2 and Al_2O_3 are not greater than 80mol% and 15mol%, respectively, and when B_2O_3 and MgO are not smaller than 6mol% and 3mol%, respectively. The solubility is unchanged even when CaO, SrO, and BaO are added up to 8mol%, 1mol%, and 1mol%, respectively.

More specifically, less than 65 mol% of SiO_2 undesirably lowers the strain point while more than 75 mol% of SiO_2 inappropriately increases a viscosity of the glass composition. Less than 6 mol% of B_2O_3 results in a decrease of solubility while more than 11 mol% of B_2O_3 results in lowering a fluoric acid proof. Exceeding the range between 5 mol% and 15mol% of Al_2O_3 brings about a reduction of the strain point and gives rise to devitrification, respectively. Less than 3 mol% of MgO increases the viscosity while more than 15 mol% of MgO brings about the devitrification in the glass substrate. Likewise, more than 8 mol% of CaO results in the devitrification.

Both SrO and BaO may be added in the form of $Ba(NO_3)_2$ and $Sr(NO_3)_2$ and effective to improve the refining property even when only 0.1 mol% is added, to suppress tendency of the devitrification and phase separation. However, more than 0.4 mol% of SrO and more than 0.2 mol% of BaO result in an increase of the viscosity and deteriorate the devitrification. As_2O_3, Sb_2O_3, and SnO_2 serve as refining agents but an excessive amount of As_2O_3 causes an environmental pollution to occur, as mentioned in the preamble of the instant

specification, while excessive amounts of Sb_2O_3 and SnO_2 result in a reduction of the strain point.

In order to improve a property of withstanding environments, no addition of As_2O_3 may be added to the glass.

The glass substrate can be manufactured by a down drawing method, a flowing method, or the like, as known in the art. In other words, the glass composition mentioned above can be readily shaped into a plate for the liquid crystal panel by the use of the conventional down drawing method, flowing method, or the like.

Referring to Fig. 1, a liquid crystal display is schematically and partially illustrated which has a pair of glass substrates 11 mentioned above. The glass substrates 11 are opposed to each other with an inside gap left therebetween. The inside gap is sealed by a sealing agent 14 and is supported by spacers 15 located within the inside gap. On each surface of the glass substrates 11 faced to the inside gap, an electrode film 12 and an alignment film 13 are successively deposited by a CVD or the like.

Practically, the electrode film 12 may form a transistor, a diode, and/or a picture element electrode in an active matrix LCD and may be a transparent film in a simple matrix LCD.

Within the inside gap, a liquid crystal layer 16 is interposed between the alignment films 13. On each outside surface of the glass substrates 11, a polarizer film 17 is located.

Such a liquid crystal display is manufactured by preparing each glass substrate 11 with the electrode film 12 and the alignment film 13, applying the sealing agent 14, and positioning the spacers 15. Thereafter, both the glass substrates 11 are assembled together and are bonded by the sealing agent 14.

CLAIMS

1. A glass composition for use as a glass substrate in a liquid crystal panel, the glass composition having a specific modulus not smaller than 31 GPa and a strain point not lower than 680℃, where the specific modulus is given by a ratio of Young's modulus to specific gravity.

2. A glass composition as claimed in claim 1, wherein the Young's modulus is not smaller than 76 GPa while the specific gravity is not higher than 2.45.

3. A glass composition as claimed in claim 1, wherein the strain point is not lower than 690 ℃ while the specific gravity and the Young's modulus are not greater than 2.42 and not smaller than 77GPa, respectively.

4. A glass composition as claimed in any one of claims 1 through 3, comprising, by mol %, 65-75% of SiO_2, 6-11% of B_2O_3, 5-15% of Al_2O_3, 3-15% of MgO, 0-8% of CaO, 0-1% of SrO, 0-1% of BaO, 0-1% of As_2O_3, 0-1% of Sb_2O_3, and 0-1% of SnO_2.

5. A glass composition as claimed in claim 4, comprising, by mol%, 67-72% of SiO_2, 6-10% of B_2O_3, 9-15% of Al_2O_3, 3-13.5% of MgO, 0-6% of CaO, 0-0.4% of SrO, 0-0.2% of BaO, 0-0.5% of As_2O_3, 0-0.5% of Sb_2O_3, 0-0.5% of SnO_2, As_2O_3+Sb_2O_3+SnO_2 falling within a range between 0 and 1%.

6. A glass composition as claimed in claimed in claim 5, comprising, by mol%, 68-72% of SiO_2, 7-9% of B_2O_3, 9-13% of Al_2O_3, 5-13.5% of MgO, 0-3.4% of CaO, 0-0.4% of SrO, and 0-0.1% of BaO.

7. A glass composition as claimed in any one of claims 4 through 6, wherein SiO_2+Al_2O_3+B_2O_3+MgO+CaO is not smaller than 97 mol%.

8. A glass composition as claimed in claim 7, wherein SiO_2+Al_2O_3+B_2O_3+MgO+CaO is not smaller than 98.5 mol%.

9. A glass composition as claimed in any one of claims 4 through 8,

wherein Al_2O_3+MgO+CaO is not smaller than 20 mol% while (Al_2O_3+MgO+CaO)/(SiO_2+B_2O_3) is not lower in mol ratio than 0.25.

10. A glass composition as claimed in claim 9, wherein Al_2O_3+MgO+CaO is not smaller than 20 mol% while a mol ratio of Al_2O_3/B_2O_3 falls within a range between 1.1 and 2.2 and another mol ratio of (Al_2O_3+MgO+CaO)/(SiO_2+B_2O_3) is not smaller than 0.25.

11. A glass composition as claimed in any one of claims 1 through 10, the glass composition being substantially free from As_2O_3.

12. A glass composition as claimed in any one of claims 1 through 11, the glass composition being substantially free from alkali metal oxide.

13. A glass composition as claimed in any one of claims 1 through 14, having a thermal expansion coefficient not greater than 35x 10^{-7}/°C, within a temperature between 100 and 300°C.

14. A glass composition for use as a glass substrate in a liquid crystal panel, the glass composition being such that a total amount of SiO_2, B_2O_3, Al_2O_3, MgO, and CaO is not less than 97 mol% and that a strain point is not lower than 680 °C and a Young's modulus is not smaller than 76GPa.

15. A glass composition as claimed in claim 14, wherein Al_2O_3+MgO+CaO is not less than 20 mol% and a mol ratio of (Al_2O_3+MgO+CaO)/(SiO_2+B_2O_3) is not smaller than 0.25.

16. A glass composition as claimed in claim 14 or 15, comprising, by mol%, 67-71% of SiO_2, 6-10% of B_2O_3, 9-15% of Al_2O_3, 3-13.5% of MgO, 0-6% of CaO, 0-0.4% of SrO, 0-0.2% of BaO, 0-0.5% of As_2O_3, 0-0.5% of Sb_2O_3, and 0-0.5% of SnO_2, (As_2O_3+Sb_2O_3+SnO_2) falling within a range between 0 and 1 mol%.

17. A glass composition for use as a glass substrate in a liquid crystal panel, the glass composition comprising, by mol%, 65-75% of SiO_2, 6-11% of B_2O_3, 5-15% of Al_2O_3, 3-15% of MgO, 0-8% of CaO, 0-1% of SrO, 0-1% of BaO,

0-1% of As_2O_3, 0-1% of Sb_2O_3, and 0-1% of SnO_2, (Al_2O_3+MgO+CaO) falling within a range between 20 and 25 % while a mol ratio of (Al_2O_3)/(B_2O_3) resides in a range between 1.1 and 1.2, (SiO_2+B_2O_3+Al_2O_3+MgO+CaO) being not less than 97 mol% while a mol ratio of (Al_2O_3+MgO+CaO)/(SiO_2+B_2O_3) is not smaller than 0.25.

18. A liquid crystal panel comprising a pair of glass substrates each of which is formed by the glass composition claimed in any one of claims 1 through 17 and which is opposed to each other with an inside gap left therebetween, the liquid crystal panel comprising an electrode film and an alignment film on an opposed surface of each of the glass substrates faced to the inside gap and a liquid crystal filled in the inside gap.

19. A liquid crystal display comprising the liquid crystal panel claimed in claim 18 and a drive circuit connected to the liquid crystal panel.

20. A method of manufacturing the glass composition claimed in any one of claims 1 through 17, comprising the step of:

shaping molten glass into a plate to form the glass substrate by down drawing or flowing.

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FIG.1